



(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

EP 0 990 732 A2

(12)

## EUROPEAN PATENT APPLICATION

(43) Date of publication:  
05.04.2000 Bulletin 2000/14

(51) Int. Cl.<sup>7</sup>: D06P 5/30, D06P 1/46,  
D06P 3/54

(21) Application number: 99111166.7

(22) Date of filing: 08.06.1999

(84) Designated Contracting States:  
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE**

Designated Extension States:

**AL LT LV MK RO SI**

(30) Priority: 01.10.1998 JP 27961098

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### (54) Textile suitable to ink jet dyeing and ink jet dyeing method

(57) A textile, to which woolen particles are attached with or without a binder, is suitably used in ink jet dye printing using a dye ink. This textile allows vivid and clear patterns to be printed on the textile by an ink jet printer, while preventing blur, colour separation, interference fringes, and deterioration of dye density on the surface of the textile. An ink jet dyeing method using such a textile includes the steps of applying a solution containing woolen particles with or without a binder onto a textile, drying the textile, printing a desired pattern on the textile by an ink jet printing technique using a dye ink, and applying heat treatment to the printed textile.

**Description**

[0001] The present invention claims a priority based on Japanese Patent Application No. H10-279610, the contents of which are incorporated hereinto by reference in its entirety.

**BACKGROUND OF THE INVENTION****1. Field of the Invention**

[0002] This invention relates to a textile suitable to ink jet dyeing, and to an ink jet dyeing method using such a textile.

**2. Description of the Related Art**

[0003] In recent years, textile printing techniques using ink jet printers for paper copies have been studied. By using such an ink jet printer, a step for making tracing plates and a step for preparing transfer paper, which are required in the conventional printing techniques for printing patterns on cloths or textiles, can be eliminated. In addition, various patterns with various colours can be easily printed on textiles.

[0004] However, with the current ink jet dyeing techniques, dye-ink droplets injected from the nozzles of the printer diffuse and blur on the surface of the textile, and in addition, the dye-ink penetrates and diffuses into the texture of the cloth. This may result in a reduced colour density on the surface of the textile and nonuniform mixture of colours. In addition, colour separation is likely to be caused in the colour-blended areas. For these reasons, the conventional textile printing techniques cannot produce vivid patterns with a high chromodensity on cloths.

[0005] In order to prevent the undesirable blur or colour separation, it has been proposed to apply several types of pretreatment to textiles prior to the ink jet dyeing (or printing) process. For example, Japanese Patent Examined Publication No. 63-31594 discloses a technique for applying a compound selected from a group consisting of a soluble macromolecule, a soluble saline, and a water-insoluble inorganic particles, all of which are chromophobe to the dye to be used, onto a textile. Japanese Patent Examined Publication No. 62-45359 teaches that a nitrogen-contained cationic substance is applied to a textile in advance if an ink containing a water-insoluble dye is used. Japanese Patent Examined Publication No. 63-31593 discloses that the viscosity and the surface tension of a dye ink are defined within certain ranges, and that the repellency of a textile is equal to or greater than 50 percent.

[0006] However, if a chromophobe compound is applied to a textile, the surface of the textile is coated with a chromophobe layer, which prevents the dye from efficiently colouring the textile. With this method, the dye density on the surface of the textile is greatly reduced. With another technique, the nitrogen-contained cationic substance can cause the water-insoluble dye molecules to cohere on the textile, thereby prevent blur and achieving high colour density on the textile. However, if the dot of the dyed portion is observed through a microscope, the dot is somewhat deformed because the water-insoluble dye flows along the direction of fiber of the textile before the cohesion. Since ink dots of a true circle cannot be obtained, the printed image is likely to deform, with fine lines appearing on the entire image, and unsmooth edge lines of the image become conspicuous. Thus, the quality of the printed image is dissatisfaction. With the third method, although a textile having a repellency of greater than 50 percent can efficiently prevent ink blurs, the diameter of the ink dot becomes too small, and therefore, each dot in the printed image becomes conspicuous. The image consisting of smaller dots gives an impression that the dye density on the surface of the textile is reduced. This method also fails to produce a high-quality printed image.

[0007] Furthermore, none of these conventional techniques can reliably prevent interference fringes (or moire fringes) from appearing on the surface of the printed textile.

**SUMMARY OF THE INVENTION**

[0008] Therefore, it is an object of the invention to overcome these problems in the prior art, and to provide a textile suitable to an ink jet dyeing process, which allows vivid and high-quality colour patterns to be printed on the textile. It is another object of the invention to provide an ink jet dyeing method using such a textile. The textile and the ink jet dyeing method according to the invention can prevent blur, colour separation, interference fringes, and reduction of the dye density.

[0009] The inventors found, after the thorough study, that if woolen particles which have both a water absorbency and an oil absorbency are attached to the surface of a textile, a vivid and clear image can be printed on the textile by an ink jet dye printing method.

[0010] The woolen particles attached to the textile are essential to the present invention. Although the permeation mechanism during the dye printing has not been clearly understood, the inventors infer that when an ink droplet is dropped on the textile having woolen particles, the water component of the ink is absorbed and held by the woolen par-

ticles having a water absorbency, and a portion of the absorbed water moves into the texture of the textile directly below the woolen particle. The organic solvent contained in the ink is also absorbed by the woolen particles because of their oil absorbency, and a portion of the oil solvent penetrates into the texture of the textile directly above the woolen particle. Accordingly, the ink does not flow along the fiber flux of the textile, and blurs are efficiently prevented. In addition, because major portion of the ink droplet is held by the woolen particles, it does not penetrate and diffuse deep inside the textile. Consequently, a high dye density is maintained on the surface of the textile, with the dot shape close to a true circle; and clear patterns with vivid colours can be produced on the textile. In addition, interference fringes and colour separations are also prevented by attaching woolen particles onto the textile. Because both the water component and the organic solvent are absorbed by the woolen particles, colours will not transfer to other cloths even if the printed textile touches some other cloths or materials.

[0011] It is preferable that the water absorbency of the woolen particle falls within the range of from 170 mL/100g to 350 mL/100g, the oil absorbency of the woolen particle is in the range from 80 mL/100g to 200 mL/100g, and the ratio of the water absorbency to the oil absorbency of the woolen particle is from 2.0 to 4.0. In this case, a very clear and vivid colour image is printed on the textile.

[0012] Preferably, the woolen particles are amorphous particles. In this case, the textile can have a better chromogenic ability, and the shape of the dot becomes close and closer to a true circle. As a result, a vivid and clear printed image can be produced.

[0013] Preferably, the woolen particles are attached to the surface of the textile by a binder. Since the woolen particles adhere on the textile, the woolen particles reliably stay on the textile until and after the dye printing.

[0014] The binder is preferably made of one or more compounds selected from a group consisting of a soluble macromolecule, a water-absorptive resin, a wax agent, and a solid surfactant.

[0015] Preferably, the diameter of the woolen particle is in the range of from 0.05 µm to 100 µm. This range allows the ink to be quickly and sufficiently absorbed during the ink jet printing, and allows the ink to be firmly maintained on the textile during a thermal treatment after the printing process.

[0016] The quantity of the woolen particles attached to the textile is preferably in the range of from 5 g/m<sup>2</sup> to 20 g/m<sup>2</sup>. This range can reliably prevent blur, colour separation, interference fringes, and reduction of the dye density on the surface of the textile.

[0017] In another aspect of the invention, an ink jet dyeing method comprises the steps of applying a solution containing woolen particles together with or without a binder onto a textile; drying the textile after the application of the solution containing the woolen particles; printing a desired pattern by an ink jet printing technique using a printing dye; and applying heat treatment to the printed textile.

[0018] With this method, by attaching the woolen particles to the textile, undesirable blur, colour separation, interference fringes, and reduction of the dye density are prevented during the ink jet dye printing process. Thus, a textile bearing a high-quality printed pattern can be produced at a low cost.

[0019] If the solution contains a binder, the woolen particles can reliably adhere to the textile, and a stable quality of the textile can be guaranteed.

[0020] The above and other objects, features, and advantages of the invention will be apparent from the following detailed description of the preferred embodiments.

#### 40 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0021] The preferred embodiments of the invention will now be described. The essential feature of the present invention is that woolen particles are attached to a textile. The types and shapes of wools which are the raw materials of the woolen particles used in this invention are not limited. For example, virgin wool, wasted short fiber remaining in a spinning process, or recycled woolen produces may be used as the materials of the woolen particles. In this invention, the term "wool" includes not only wool itself, but also mohair and cashmere shorn from goat and the like.

[0022] The states and types of the woolen particles are not limited. For example, fibriform woolen particles, needle-type woolen particles, and amorphous woolen particles are used. Examples of commercially available fibriform woolen particles include "MERRY POWDER N" manufactured by Kyoeisha Kagaku Kabushiki Kaisha. A commercially available amorphous woolen particle is, for example, "MERRY POWDER 30" manufactured by Kyoeisha Kagaku Kabushiki Kaisha. Amorphous particles are particles which do not have a specific shape, unlike the fiberiform particle or needle particles. The amorphous particles are generally observed through a microscope.

[0023] Woolen particles are generally produced by a physical/mechanical treatment or a chemical/mechanical treatment. Examples of the physical/mechanical treatment include low-temperature grinding of moulded wool fibers (disclosed in Japanese Patent Laid-open Publication No. 55-84556), and cyclic vacuum grinding using a special cyclic vacuum grinder (disclosed in Japanese Patent Laid-open Publication No. 62-283310). Examples of the chemical/mechanical treatment include mechanical grinding after enzymatic deterioration of wool fibers (disclosed in Japanese Patent Laid-open Publication No. 4-89836), and mechanical grinding after successive steps of chemical treatment

wool fibers using an oxidizing agent or a reducer, lubrication, and drying (disclosed in Japanese Patent Laid-open Publication No. 6-192433).

[0024] It is preferred that amorphous woolen particles are used because the shape of the ink dot injected onto the textile becomes close to a true circle, and as a result, the print quality on the textile is improved. Such amorphous woolen particles are produced by, for example, an above-described chemical/mechanical treatment.

[0025] It is preferable that the water absorbency of the woolen particle is in the range from 170 mL/100g to 350 mL/100g, the oil absorbency of the woolen particle is in the range from 80 mL/100g to 200 mL/100g, and the ratio of the water absorbency to the oil absorbency of the woolen particle is from 2.0 to 4.0. If the water absorbency is less than 170 mL/100g, blue can not be efficiently prevented. If the water absorbency exceeds 350 mL/100g, the ink dye can not move into the texture of the textile, and the printed image becomes unstable. If the oil absorbency is below 80 mL/100g, a sufficient anti-blur effect can not be achieved, and in addition, the dye and the organic solvent are likely to bleed onto the surface of the textile as time passes. If the oil absorbency exceeds 200 mL/100g, the ink dye can not move into the texture of the textile. If the ratio of the water absorbency to the oil absorbency is smaller than 2.0, the organic solvent in the ink is likely to bleed to the surface of the textile, which may cause colour separation. With the ratio above 4.0, the water component of the ink tends to diffuse, which causes the printed image to be blurred. The oil absorbency (mL/100g) was measured based on the JIS K5101 standard. In measurement, boiled linseed oil was gradually dropped onto 3g sample particles by a buret. When the sample changed its state from pâté (paste) to the fluid state, the total amount of dropped oil was measured, and the corresponding oil absorbency for 100g sample was calculated. The water absorbency (mL/100g) was measured in the same manner except that water was used in place of the boiled linseed oil.

[0026] It is preferred that the diameter of the woolen particle is in the range of from 0.05 µm to 100 µm, but not limited to this range. If the diameter of the woolen particle is smaller than 0.05 µm, the woolen particle can not have a sufficient ink-absorptive ability. Above 100 µm, the surface of the textile becomes uneven, and the ink-absorbency varies. This may partially prevent the dye contained in the ink from moving into the texture of the textile, and cause blur in the printed image. Therefore, it is more preferable that the diameter of the woolen particles falls within the range of from 0.5 µm to 50 µm.

[0027] The preferred quantity of the woolen particles attached to the textile is in the range of from 5 g/m<sup>2</sup> to 20 g/m<sup>2</sup>. Below 5 g/m<sup>2</sup>, the effect of the woolen particles can not be sufficiently exhibited. Above 20 g/m<sup>2</sup>, the touch of the printed textile becomes dissatisfaction. It is more preferred to set the range from 7 g/m<sup>2</sup> to 15 g/m<sup>2</sup> because this range can reliably prevent blur, colour separation, and interference fringes, while keeping the dye density on the surface of the textile high. The quantity of the woolen particle described above is the value measured after the textile was dried.

[0028] Preferably, the woolen particles are attached to the textile by a binder. The binder enhances the adhesion of the woolen particles to the textile, and the woolen particles reliably stay on the textile until and after the dye printing. Thus, the quality of the printed products becomes stable.

[0029] Any suitable binders can be used as long as the woolen particles are attached to the textile. For example, a soluble macromolecule, a water-absorptive resin, a wax agent, and a solid surfactant are preferably used. Among them, soluble macromolecule is especially preferred because this binder is easily removed when the printed textile is rinsed after the ink jet dye-printing for the purposes of removing the non-fixed dye. However, the printed textile does not necessarily have to be rinsed. The printed products may be shipped without rinsing.

[0030] The soluble macromolecule may be either a natural macromolecule or a synthetic macromolecule. Examples of the natural soluble macromolecule include, but not limited to, starchy substances, such as corn powder and flour; cellulose substances, such as carboxymethyl cellulose and hydroxyethylcellulose; polysaccharide, such as sodium alginate, gum arabic, locust bean gum, and guar gum; and protein, such as gelatine and casein. Examples of the synthetic soluble macromolecule include, but not limited to, polyvinyl alcohol, polyethylene oxide compound, soluble macromolecules of acrylic acid group, and soluble macromolecules of maleic anhydride.

[0031] Examples of the water-absorptive resin include, but not limited to, bridged starch, bridged cellulose, bridged acrylate, bridged polystyrene, bridged acrylic acid-acrylamide copolymer, and bridged isobutylene-maleic anhydride copolymer.

[0032] Examples of the wax agent include, but not limited to, hydrocarbon, such as paraffin wax; higher alcohol, such as cetylalcohol; higher fatty acid, such as myristic acid; and higher fatty acid alcohol ester, such as beeswax (animal wax) and carnauba (plant wax).

[0033] Examples of solid surfactant include, but not limited to, nonionic surfactant of ether type, ester type, etherester type, and nitrogen-containing type; anion surfactant of carbonate (soap) type, sulfonate type, ester sulfate type, and ester phosphate type; cationic surfactant of aliphatic amine salt, and aliphatic quaternary ammoniate; and amphi-ionic surfactant of betaine type, and amino carbonate type. A solid surfactant is defined as a surfactant which is in the solid state at a room temperature (25°C).

[0034] The preferred quantity of the binder is 1-200 weight parts with respect to the woolen particles of 100 weight parts. Below 1 weight part, a sufficient bonding effect can not be obtained. Above 200 weight parts, the amount of the binder becomes too much relative to the woolen particles, which prevents the effect of the woolen particles. More pre-

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ferred quantity of the binder is 10-100 weight parts with respect to the woolen particles of 100 weight parts.

[0035] Any textiles can be used in this invention as long as they are dyed by ink dyes. For example, polyester, cotton cloth, nylon, wool, silk, and acryl are used. To dye polyester cloth, disperse dye is generally used. For cotton cloth, reactive dye is used, and in general, acid dye is used for nylon, wool, and silk. Although the types of dyes and cloths are not necessarily limited to these combination, it is preferred to use disperse dye and polyester textile because woolen particles are chromophobe with respect to disperse dyes, and because polyester fiber has excellent dyeing characteristics (such as colouring uniformity, colorfastness, vividness) with respect to disperse dyes. In this case, a clear and vivid print image can be obtained by ink jet printing using a disperse dye.

[0036] In order to produce a textile suitable to ink jet printing, woolen particles or a combination of woolen particles and a binder is used in the form of aqueous emulsion or solution. Such solution is applied to the textile by various methods, such as padding, spraying, immersion, coating, ink jetting, etc., and after the application of the solution, the textile is dried. Since the viscosity of the solution containing the woolen particles is relatively low, a pad method or a spray method is preferably used. If a binder is used together with the woolen particles, the woolen particles and the binder are uniformly mixed in the solution, and applied to the textile simultaneously. In this case, the adhesion of the woolen particles is increased.

[0037] The textile coated with the woolen particles (with or without the binder) exhibits excellent printing properties in ink jet dye printing, and clear and vivid colour patterns can be printed on the textile, keeping a high colour density on the surface of the textile. Although the dyeing mechanism is not totally clear, it is inferred that when the ink-dye droplets are injected from the nozzles of the ink jet printer onto the textile coated with the woolen particles, the water component of the ink is absorbed and held by the woolen particles having a water absorbency, and a portion of the absorbed water moves into the texture of the textile directly below the woolen particle. The organic solvent contained in the ink is also absorbed by the woolen particles because of their oil absorbency, and a portion of the oil solvent penetrates into the texture of the textile directly above the woolen particle. Accordingly, the ink does not flow along the fiber flux of the textile, and blur is efficiently prevented. In addition, because major portion of the ink droplet is held by the woolen particles, it does not penetrate and diffuse deep inside the textile. Consequently, a high dye density is maintained on the surface of the textile, with the dot shape close to a true circle, and clear patterns with vivid colours can be produced on the textile. In addition, interference fringes and colour separations are also prevented by attaching woolen particles onto the textile. Because both the water component and the organic solvent are absorbed by the woolen particles, colours will not transfer to other cloths even if the printed textile touches some other cloths or materials.

[0038] Any ink jet printing methods are preferably used to dye-print the textile. For example, thermal ink jet printing, piezoelectric ink jet printing, and charge-control ink jet printing techniques are used.

[0039] The ink used in the ink jet printer is a dye ink. The diameter of the dye particle is preferably less than 1 $\mu\text{m}$ . Various additives, such as a disperser, a surface-tension adjusting agent, and an anti-dry agent, may be added to the ink.

[0040] The viscosity of the dye ink is preferably set to the range of 2-10 cps (at 25°C). Below 2 cps, the ink dot may blur on the textile. Above 10 cps, the ink can not be injected stably due to the high viscosity. The surface tension of the ink is preferably set to the range of 30-60 mN/m. Below 30 mN/m, the ink injection condition becomes bad, and blur may be caused. Above 60 mN/m, the ink injection condition becomes bad, and the dot diameter becomes too small, which is undesirable for dye printing.

[0041] After the dye printing, the printed textile is subjected to a thermal treatment for purposes of fixing the dye on the textile and improving the vividness. If a wax agent is used as the binder, the wax agent melts into the dye, and causes migration, whereby an appropriate dot diameter which corresponds to the resolution of the ink jet printer is maintained on the textile. By keeping the appropriate dot diameter, interference fringes are reliably prevented, and a high-quality printed image is produced. The thermal treatment is performed at about 110-190°C for about 1-10 minutes. Examples of the thermal treatment include, but not limited to, high-pressure steam treatment, high-temperature steam treatment, and dry heating.

[0042] After the heat treatment, little unfixed dye remains on the textile, and almost no stains are caused. Accordingly, the printed textiles may be shipped after the heat treatment, or may be rinsed before shipping if necessary. Since the dye component contained in the ink was well fixed to the textile by the heat treatment, there is little likelihood that the dye will dissolve into the water during the rinse and stain the textile. In addition, it is not necessary for the rinsing process to require any special sewage treatments.

[0043] Next, actual examples and comparison examples will be exhibited below. The inks and their components used in the ink jet dyeing are as follows:

(Disperse dye ink)

[0044]

<b>*YELLOW</b>			
C.I. Disperse Yellow 42	<b>7.0 weight parts</b>		
anionic disperser	<b>2.0 weight parts</b>		
propylene glycol	<b>30.0 weight parts</b>		
ion-exchange water	<b>61.0 weight parts</b>		
<b>*MAGENTA</b>			
C.I. Disperse Red 283	<b>6.0 weight parts</b>		
anionic disperser	<b>11.5 weight parts</b>		
propylene glycol	<b>30.0 weight parts</b>		
ion-exchange water	<b>62.5 weight parts</b>		
<b>*CYAN</b>			
C.I. Disperse Blue 60	<b>5.0 weight parts</b>		
anionic disperser	<b>2.0 weight parts</b>		
propylene glycol	<b>30.0 weight parts</b>		
ion-exchange water	<b>63.0 weight parts</b>		
<b>*BLACK</b>			
C.I. Disperse Orange 30	<b>3.0 weight parts</b>		
C.I. Disperse Red 167	<b>1.5 weight parts</b>		
C.I. Disperse Blue 73	<b>6.0 weight parts</b>		
anionic disperser	<b>3.0 weight parts</b>		
propylene glycol	<b>30.0 weight parts</b>		
ion-exchange water	<b>56.5 weight parts</b>		

40 (Example 1) A pretreatment solution which contains 10 wt% MERRY POWDER 30 (manufactured by Kyoeisha Kagaku) was prepared. MERRY POWDER 30 consists of amorphous woolen particles having an average diameter of 8.8 µm.

45 A pretreatment solution which contains 10 wt% MERRY POWDER 30 (manufactured by Kyoeisha Kagaku) was prepared. MERRY POWDER 30 consists of amorphous woolen particles having an average diameter of 8.8 µm. The water absorbency of MERRY POWDER 30 was 301 mL/100g; the oil absorbency was 104 mL/100g, and the ratio of water absorbency-to oil absorbency was 2.90. This solution was applied to polyester cloth (122 g/m<sup>2</sup>) by an ordinary pad method so that the pick-up ratio became 83%. Then, the polyester cloth was dried at 120°C for 10 minutes. A pattern was printed on the treated polyester cloth by a piezoelectric ink jet printer using disperse dye inks of four colours (yellow, magenta, cyan, and black). Heat treatment was applied to the printed cloth at 190°C for 5 minutes to fix the dyes. Then, the textile was rinsed by ordinary reductive rinse:

50 (Example 2)

55 A pretreatment solution which contains 10 wt% MERRY POWDER 30 (the same product as used in Example 1) and 4 wt% Cell-base gum CRM (carboxymethylcellulose) manufactured by Dicel Kagaku Kabushiki Kaisha was prepared. The other steps and conditions for producing a printed textile were the same as Example 1.

## (Example 3)

[0047] A pretreatment solution which contains 10wt% wool powder and 4 wt% Cell-base gum CRM was prepared. The wool powder consists of amorphous woolen particles having an average diameter of 9.5 µm. The water absorbency of the wool powder was 307 mL/100g, the oil absorbency was 98.6 mL/100g, and the ratio of water absorbency to oil absorbency was 3.11. The other steps and conditions were the same as in Example 1.

## (Example 4)

[0048] A pretreatment solution which contains 12 wt% wool powder manufactured by Daiwabo Polytech Co., Ltd. and 4 wt% Cell-base gum CRM was prepared. The wool powder used in this example consists of fibriform woolen particles having an average diameter of 10 µm. The water absorbency of the wool powder was 176 mL/100g, the oil absorbency was 81 mL/100g, and the ratio of water absorbency to oil absorbency was 2.18. The other steps and conditions were the same as in Example 1.

## (Example 5)

[0049] A pretreatment solution which contains 7 wt% MERRY POWDER 30 and 2 wt% JIP500 (water-absorptive resin of poly acrylic acid) manufactured by Sanyo-Kasei-Kabushiki Kaisha was prepared. The other steps and conditions were the same as in Example 1.

## (Example 6)

[0050] A pretreatment solution which contains 16 wt% MERRY POWDER 30 and 6 wt% Lipo-oil NT12 (wax emulsion containing paraffin wax and fatty ester) manufactured by Nikka Kagaku Kabushiki Kaisha was prepared. The other steps and conditions were the same as in Example 1.

## (Example 7)

[0051] A pretreatment solution which contains 8 wt% MERRY POWDER 30 and 4 wt% Marseilles soap (solid surfactant of vegetable oil sodium carbonate group) manufactured by Lion Kabushiki Kaisha was prepared. The other steps and conditions were the same as in Example 1.

[0052] These examples are shown in TABLE 1.

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TABLE 1.

MERRY POWDER 30: water-absorbency 301 (mL/100 g), oil-absorbency 104 (mL/100 g)  
water-absorbency/oil-absorbency = 2.90

WOOL POWDER (amorphous) : water-absorbency 307 (mL/100 g), oil-absorbency 98.6 (mL/100 g)  
 water-absorbency/oil-absorbency = 3.11

WOOL POWDER : water-absorbency 176 (mL/100 g), oil-absorbency 81 (mL/100 g)  
 (fibriform) water-absorbency/oil-absorbency = 2.18

(Comparison Example 1)

[0053] A colour pattern was printed on non-treated polyester cloth by an ink jet printer. The printed cloth was subjected to heat treatment and reductive rinse, as in Example 1.

(Comparison Example 2)

[0054] A pretreatment solution which contains 9 wt% Cell-base gum CRM was prepared and applied to the polyester cloth. The other steps and conditions for producing a printed textile were the same as Example 1.

(Comparison Example 3)

[0055] A pretreatment solution which contains 10 wt% feather powder manufactured by Ishiwara Chemicals Co., Ltd. and 4 wt% Cell-base gum CRM (carboxymethylcellulose) was prepared and applied to the polyester cloth. The feather powder consists of feather particles having an average diameter of 8.7 µm. The other steps and conditions were the same as in Example 1.

(Comparison Example 4)

[0056] A pretreatment solution which contains 10 wt% superfine silk powder manufactured by Daiwabo Polytech Co., Ltd. and 4 wt% Cell-base gum CRM was prepared and applied to the polyester cloth. The superfine silk powder consists of silk fibroin particles having an average diameter of 9 µm. The other steps and conditions were the same as in Example 1.

(Comparison Example 5)

[0057] A pretreatment solution which contains 10 wt% TRIAZET CX manufactured by Showa Denko Kabushiki Kaisha and 4 wt% cell-base gum CRM was prepared and applied to the polyester cloth. TRIAZET CX consists of collagen particles having an average diameter of 5 µm. The other steps and conditions were the same as in Example 1.

(Comparison Example 6)

[0058] A pretreatment solution which contains 10 wt% cotton powder manufactured by Daiwabo Polytech Co., Ltd. and 4 wt% Cell-base gum CRM was prepared and applied to the polyester cloth. The cotton powder consists of cotton particles having an average diameter of 12 µm. The other steps and conditions were the same as in Example 1.

(Comparison Example 7)

[0059] A pretreatment solution which contains 10 wt% FINE SEAL X45 manufactured by Tokuyama Co., Ltd. and 4 wt% Cell-base gum CRM was prepared and applied to the polyester cloth. FINE SEAL X45 consists of amorphous silica particles having an average aggregation diameter of 4.5 µm. The other steps and conditions were the same as in Example 1.

(Comparison Example 8)

[0060] A pretreatment solution which contains 9 wt% NEOFIX RP70 manufactured by Nikka Kagaku Kabushiki Kaisha was prepared and applied to the polyester cloth. NEOFIX RP70 contains polyethylene polyamine-type cationic resin of 70 wt%. The other steps and conditions were the same as in Example 1.

(Comparison Example 9)

[0061] A pretreatment solution which contains 3 wt% Asahi Guard AG-850 manufactured by Meisei Kagaku Kabushiki Kaisha was prepared and applied to the polyester cloth. Asahi Guard AG-850 contains fluorine-type water repellent of 30 wt%. The other steps and conditions were the same as in Example 1.

[0062] These comparison examples are shown in TABLE 2.

TABLE 2

		COMPARISON EXAMPLE								
		1	2	3	4	5	6	7	8	9
		COMPOSITION OF SOLUTION (Wt%)								
Cell base gum CRM	-	9	4	4	4	4	4	4	-	-
Feather particles	-	-	10	-	-	-	-	-	-	-
Silk particles	-	-	-	10	-	-	-	-	-	-
Collagen particles	-	-	-	-	10	-	-	-	-	-
Cotton particles	-	-	-	-	-	10	-	-	-	-
Amorphous silica particles	-	-	-	-	-	-	10	-	-	-
NEOFIX RP70	-	-	-	-	-	-	-	-	9	-
ASAHI GUARD AG850	-	-	-	-	-	-	-	-	-	3
Amount of woolen particles applied to textile (g/m <sup>2</sup> ; in dry state)	9	14	14	14	14	14	14	14	14	1
Water-absorbency (mL/100 g)	130	180	192	233	390					
Oil-absorbency (mL/100 g)	300	70	69	126	280					
Water-absorbency/oil-absorbency	0.43	2.57	2.77	1.85	1.39					

[0063] The qualities of the printed textiles obtained from Examples 1-7 and Comparison Examples 1-9 were evaluated comprehensively by observing blur as a whole, the dot diameter of the dye ink, the shape of the ink dot, colour separation in the colour blended area, the chromogenic ability, stains, and interference fringes. The evaluation results are

shown in Tables 3 and 4.

[0064] Among the above-described items, blur, colour separation, stains, and interference fringes were graded by 4-grade evaluation, that is, "none", "light", "medium" and "heavy". The stains, the average dot diameter, the degrees of true-circle, and chromogenic ability (dye density) were evaluated according to the following criteria.

5 (Stains)

[0065] Immediately after the dye-printing (and before the heat treatment), another piece of cloth of the same material was put over the printed area, and weighted with a 500 g weight having a diameter of 100 mm for a minute. Then, the 10 stains on the upper cloth were observed by eyes, and evaluated by the 4 grades (none, light, medium, and heavy).

(Average Dot Diameter)

[0066] The average diameter of the ink dot was calculated after the heat treatment and rinse. The smaller the dot 15 diameter, the less the blur. However, if the dot diameter is too small, the dots in the printed image become conspicuous, and it appears that the dye density is deteriorated on the surface of the textile. If the dot diameter is too large, the printed image blurs, and a sharp and clear line can not be obtained. In either case, the print quality is unsatisfactory. With a general printer resolution (360 dpi), the optimal dot diameter is about 100  $\mu\text{m}$ .

20 (Degree of True-circle)

[0067] After the heat treatment and rinse, the longer and shorter diameters of arbitrarily selected 5 dots were measured, and the average was calculated. The degree of true circle is defined as the ratio of the longer diameter (major axis) to the shorter diameter (minor axis). The degree of true-circle represents the deformation of the ink dot from the 25 true circle. As the value approaches 1, the dot shape becomes closer to a true circle, and the resultant image quality becomes high.

(Dye density - Chromogenic Ability)

30 [0068] After the heat treatment and rinse, the brightness  $L^*$  of a part (3 cm X 3 cm) of the printed area on the textile was measured by a colorimeter (CM-3700d manufactured by Minolta). The smaller the brightness  $L^*$ , the higher the dye 35 density with a better chromogenic ability. The brightness  $L^*$  is defined by the  $L^*a^*b^*$  colour representation method (JIS Z8729-1980).

[0069] The total evaluation for the print quality was made by 5 grades, that is, excellent (◎), good (○), fair (△), 40 slightly poor (✗), and poor (✗✗).

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TABLE 3

	Blur	Average dot diameter ( $\mu\text{m}$ )	Degree of true-circle (Average)	Brightness ( $L^*$ value) (Chromogenic ability)	Color separation	Stains	Interference fringes	Evaluation
Example 1	None	108.1	1.45	47.14	None	None	None	◎
Example 2	None	107.7	1.47	47.26	None	None	None	◎
Example 3	None	108.5	1.50	47.29	None	None	None	◎
Example 4	None	110.4	1.60	47.66	None	None	None	○
Example 5	None	105.7	1.44	47.11	None	None	None	◎
Example 6	None	109.2	1.41	47.49	None	None	None	◎
Example 7	None	108.7	1.50	47.35	None	None	None	◎

TABLE 4

	Blur	Average dot diameter ( $\mu\text{m}$ )	Degree of true-circle (Average)	Brightness ( $L^*$ value) (Chromogenic ability)	Color separation.	Stains	Interference fringes	Evaluation
Comparison example 1	Heavy	175.0	3.67	50.58	Heavy	Light	None	XX
Comparison example 2	Medium	130.0	1.89	49.52	Light	Light	None	△
Comparison example 3	Heavy	143.5	2.40	47.89	Medium	Light	None	X
Comparison example 4	Light	123.7	1.78	48.75	Light	Light	None	△
Comparison example 5	Medium	128.5	2.29	49.31	Light	Light	None	X
Comparison example 6	Medium	136.6	2.10	49.38	Medium	Light	None	X
Comparison example 7	None	87.0	1.38	55.93	Heavy	None	Light	X
Comparison example 8	Light	120.0	2.69	47.46	Light	Heavy	Heavy	△
Comparison example 9	None	85.0	1.43	48.93	Heavy	Heavy	Heavy	X

[0070] As is clear from Tables 3 and 4, with the textiles of Examples 1 through 7 which were produced according to the present invention so as to be suitable to ink jet printing, the dye densities or the brightnesses of the printed image

were high, and little blur or colour separation was observed. In addition, the dot shapes were close to true circles with an appropriate range of diameter. In appearance, clear and vivid patterns were printed without interference fringes. Stains or colour transfer to other cloths were not observed.

[0071] In contrast, the textiles of Comparison Examples 1-6, and 8 were inferior in the blur prevention effect, and the printed image as a whole was not so sharp as the textiles of the present invention. Colour separation was observed at colour blended areas in the printed images. Stains or colour transfer was also observed. In Comparison Example 8, interference fringes occurred. In Comparison Examples 1, 2, and 5-7, the colour density or the brightness was dissatisfaction. Although the printed patterns were not blurred in Comparison Examples 7 and 9, colour separation and interference fringes occurred, and the dot diameters were too small (which caused the apparent brightness to be reduced).

[0072] As has been described, according to the invention, woolen particles are attached to a textile which is to be dye-printed. These woolen particles can efficiently prevent reduction of the dye density, blur, colour separation, and interference fringes, which were the problems in the conventional dye-printing techniques. As a result, a clear and vivid pattern image can be printed on a textile. The woolen particles can retain dyes stably, and therefore, stains or colour transfer to other cloths can be prevented.

[0073] If water absorbency of the woolen particle is in the range from 170 mL/100g to 350 mL/100g, the oil absorbency of the woolen particle is in the range from 80 mL/100g to 200 mL/100g, and the ratio of the water absorbency to the oil absorbency is from 2.0 to 4.0, then more preferable result can be obtained, producing a clear and vivid dye print on the textile with little blurs.

[0074] If the woolen particles are amorphous, the chromogenic ability (or the brightness) is increased, and at the same time, the dot shape approaches to a true circle. Thus, the print quality is greatly improved.

[0075] By attaching the woolen particles to a textile using a binder, the woolen particles can stably sit on the textile even after the printing and rinsing steps.

[0076] If the binder is made of one or more compounds selected from a group consisting of a soluble macromolecule, a water-absorptive resin, a wax agent, and a solid surfactant, the adhesion is increased.

[0077] By setting the diameter of the woolen particle to the range of from 0.05  $\mu\text{m}$  to 100  $\mu\text{m}$ , the woolen particles can absorb the ink promptly with little blur, and in addition, the dye contained in the ink can be efficiently fixed onto the textile by the heat treatment, whereby a stable print quality with vivid colours can be guaranteed.

[0078] The preferred quantity of the woolen particles attached to the surface of the textile is in the range of from 5 g/m<sup>2</sup> to 20 g/m<sup>2</sup>. In this case, the touch of the printed textile is excellent, while reduction of the dye density, colour separation, blurs, interference fringes are reliably prevented.

[0079] An ink jet dyeing method according to the present invention uses the textile described above. With this method, a solution containing woolen particles with or without a binder is applied to a textile. After the textile is dried, a desired pattern is printed on the textile by an ink jet printing technique using a dye ink. Then, heat treatment is applied to the printed textile. With this method, reduction of the dye density, blurs, colour separations, and interference fringes are efficiently prevented in the ink jet printing process, while high-quality printed textiles can be manufactured at a low cost. If the solution contains a binder, the adhesion of the woolen particles to the textile is guaranteed, and undesirable colour transfer from the printed pattern to other cloths is reliably prevented. Because little dye component will dissolve into the rinsing water, it is not necessary to provide any special sewage treatments.

[0080] Although the invention has been described based on the preferred embodiment, the terms and the sentences used in this specification are explanatory, and not limiting the invention. It should be appreciated that there are many modifications and substitutions without departing from the spirit and scope of the invention, which are defined by the appended claims.

## Claims

1. A textile suitable to ink jet dyeing, characterized in that woolen particles are attached to the surface of the textile.
2. The textile according to claim 1, wherein the water absorbency of the woolen particle falls within the range of from 170 mL/100g to 350 mL/100g, the oil absorbency of the woolen particle is in the range from 80 mL/100g to 200 mL/100g, and the ratio of the water absorbency to the oil absorbency is from 2.0 to 4.0.
3. The textile according to claim 1 or 2, wherein the woolen particles are amorphous particles.
4. The textile according to any one of claims 1 to 3, wherein the woolen particles are attached to the textile by a binder.
5. The textile according to claim 4, wherein the quantity of the binder is 1-200 weight parts with respect to the woolen particles of 100 weight parts.

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6. The textile according to claim 4 or 5, wherein the binder is made of one or more compounds selected from a group consisting of a soluble macromolecule, a water-absorptive resin, a wax agent, and a solid surfactant.
7. The textile according to claim 6, wherein the binder is a soluble macromolecule.
- 5 8. The textile according to any one of claims 1 to 7, wherein the diameter of the woolen particle falls within the range of from 0.05 µm to 100 µm.
- 10 9. The textile according to claim 8, wherein the diameter of the woolen particle falls within the range of from 0.05 µm to 50 µm.
- 15 10. The textile according to any one of claims 1 to 9, wherein the quantity of the woolen particles attached to the surface of the textile falls within the range of from 5 g/m<sup>2</sup> to 20 g/m<sup>2</sup>.
11. The textile according to claim 10, wherein the quantity of the woolen particles attached to the surface of the textile is in the range from 7 g/m<sup>2</sup> to 15 g/m<sup>2</sup>.
- 20 12. An ink jet dyeing method including the steps of:
  - applying a solution containing woolen particles onto a textile;
  - drying the textile after the application of the solution containing the woolen particles;
  - printing a desired pattern by an ink jet printing technique using a printing dye; and
  - applying heat treatment to the printed textile.
- 25 13. An ink jet dyeing method including the steps of:
  - applying a solution containing woolen particles and a binder onto a textile;
  - drying the textile after the application of the solution containing the woolen particles and the binder;
  - 30 printing a desired pattern by an ink jet printing technique using a printing dye; and
  - applying heat treatment to the printed textile.
14. The ink jet dyeing method according to claim 12 or 13, wherein the solution is applied to the textile using a pad method or a spray method.
- 35 15. The ink jet dyeing method according to any one of claims 12 to 14, wherein the textile is made of a polyester fiber, and the printing dye is a disperse dye.

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1. *Leucosia* *leucostoma* *leucostoma*

在這裏，我們可以說，我們的社會主義者是沒有理由對此表示不滿的。

<sup>1</sup> See also the discussion of the relationship between the concept of "cultural capital" and the concept of "cultural value" in the introduction to this volume.

Chlorophyll a fluorescence and its relationship to light absorption by phytoplankton

$$e^{-\lambda t} \left( \frac{d}{dt} e^{\lambda t} \right)^2 = e^{-\lambda t} \left( \lambda e^{\lambda t} + e^{\lambda t} \right)^2 = e^{-\lambda t} \lambda^2 e^{2\lambda t} = \lambda^2 e^{\lambda t} = \lambda^2 e^{\lambda t} \cdot e^{-\lambda t} = \lambda^2.$$

1920-1921. The first year of the new school was opened at the former site of the old school.

For the first time, we can see the effect of the new model on the growth of the economy.

தான் கூட விரைவாக நீண்ட புதிய முறைகளை விடுவது அதே நோயை விடுவது என்று சொல்ல வேண்டும்.

It is also a good idea to keep the  $\mu$  values low, as this will reduce the variance.

“The first time I saw him, he was sitting in a chair, looking at me with a very serious expression. He had a mustache and was wearing a suit jacket over a white shirt. I think he was a doctor or a scientist. He asked me some questions about my family history and then told me about his own research. It was very interesting and informative.”

在這裏，我們可以說，這就是「中國化」的問題。我們要將中國文化與西方文化合而為一，這就是「中國化」的問題。



(19) Europäisches Patentamt  
European Patent Office

Office européen des brevets



(11) EP 0 990 732 A3

(12) **EUROPEAN PATENT APPLICATION**

(88) Date of publication A3:  
09.01.2002 Bulletin 2002/02

(51) Int Cl. 7: D06P 5/30, D06P 1/46,  
D06P 3/54, D06P 5/00

(43) Date of publication A2:  
05.04.2000 Bulletin 2000/14

(21) Application number: 991111166.7

(22) Date of filing: 08.06.1999

(84) Designated Contracting States:  
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU  
MC NL PT SE

Designated Extension States:  
AL LT LV MK RO SI

(30) Priority: 01.10.1998 JP 27961098

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(54) **Textile suitable to ink jet dyeing and ink jet dyeing method**

(57) A textile, to which woolen particles are attached with or without a binder, is suitably used in ink jet dye printing using a dye ink. This textile allows vivid and clear patterns to be printed on the textile by an ink jet printer, while preventing blur, colour separation, interference fringes, and deterioration of dye density on the sur-

face of the textile. An ink jet dyeing method using such a textile includes the steps of applying a solution containing woolen particles with or without a binder onto a textile, drying the textile, printing a desired pattern on the textile by an ink jet printing technique using a dye ink, and applying heat treatment to the printed textile.



**European Patent  
Office**

## **EUROPEAN SEARCH REPORT**

**Application Number**

## **DOCUMENTS CONSIDERED TO BE RELEVANT**

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
X	PATENT ABSTRACTS OF JAPAN vol. 1995, no. 05, 30 June 1995 (1995-06-30) & JP 07 054277 A (UNITIKA LTD), 28 February 1995 (1995-02-28) * abstract *	1-11	D06P5/30 D06P1/46 D06P3/54 D06P5/00
X	DATABASE WPI Section Ch, Week 199505 Derwent Publications Ltd., London, GB; Class A23, AN 1995-033016 XP002182057 & JP 06 316871 A (UNITIKA LTD), 15 November 1994 (1994-11-15) * abstract *	1-11	
A	WO 98 07799 A (IDEMITSU PETROCHEMICAL CO ;FUKATSU FUMIOKI (JP)) 26 February 1998 (1998-02-26), & EP 0 933 411 A 4 August 1999 (1999-08-04) * paragraph '0002! * * paragraph '0016! - paragraph '0031! * * paragraph '0047! - paragraph '0054! *	1-15	TECHNICAL FIELDS SEARCHED (Int.Cl.7)  D06P
A,D	DATABASE WPI Section Ch, Week 198618 Derwent Publications Ltd., London, GB; Class A87, AN 1986-115656 XP002182058 & JP 61 055277 A1 (TORAY INDU INC), 19 March 1986 (1986-03-19) * abstract *	1-15	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	6 November 2001	Fiocco, M	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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P : intermediate document	& : member of the same patent family, corresponding document		

**ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 11 1166

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

06-11-2001

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
JP 07054277	A	28-02-1995		NONE		
JP 6316871	A	15-11-1994		NONE		
WO 9807799	A	26-02-1998	JP EP WO JP TW	9157573 A 0933411 A1 9807799 A1 10114147 A 386102 B	17-06-1997 04-08-1999 26-02-1998 06-05-1998 01-04-2000	
JP 61055277	A	19-03-1986	JP JP	1677285 C 63031594 B	13-07-1992 24-06-1988	

— 1 —

“*It is the first time that I have seen such a thing.*”